

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 685 250 A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **95108233.8**

(51) Int. Cl.⁸: **B01D 19/04, C11D 3/00,
C08L 83/08, C08L 83/06**

(22) Date of filing: **29.05.95**

(30) Priority: **30.05.94 JP 139488/94**

(43) Date of publication of application:
06.12.95 Bulletin 95/49

(84) Designated Contracting States:
BE DE ES FR GB IT NL

(71) Applicant: **Dow Corning Toray Silicone
Company, Limited
Mitsui Bldg. No. 6,
2-3-16, Nihonbashi-Muromachi,
Chuo-Ku
Tokyo 103 (JP)**

(72) Inventor: **Kondo, Hidetoshi, c/o Dow Corning
Toray Sil.Co.Ltd
Mitsui Buil. No. 6,
3-16, 2-chome
Nihonbashi-Muromachi,
Chuo-Ku,
Tokyo 103 (JP)**
Inventor: **Takahashi, Masahiro, c/o Dow
Corning Toray
Sil. Co. Ltd.,
Mitsui Buil. No. 6,
3-16, 2-chome
Nihonbashi-Muromachi,
Chuo-Ku,
Tokyo 103 (JP)**

(74) Representative: **Spott, Gottfried, Dr.
Patentanwälte
Spott, Weinmiller & Partner
Sendlinger-Tor-Platz 11
D-80336 München (DE)**

(54) **Silicone foam control compositions.**

(57) A silicone foam control composition is disclosed that is able to inhibit foaming only during the rinse stage without impairment of foaming during the wash stage. The silicone foam control composition comprises 80 to 99 weight% of an organopolysiloxane containing amino-or carboxyl-functional organic groups and silica with a specific surface area of at least 50 m²/g.

EP 0 685 250 A1

This invention relates to foam control compositions for use in detergents. More particularly, it provides foam control compositions which inhibit foaming during post-wash rinsing operations and are able to do so without impairing cleaning performance while still retaining an appropriate level of foaming during the washing stage.

- 5 Soiled clothing is cleaned by introducing the clothing, a detergent composition, and water into a washing machine. The soil becomes dispersed in the water through the action of mechanical force and affinity with the surfactant. The resulting waterborne soil dispersion is then discharged, and residuals are subsequently rinsed out with fresh water. However, due to the strong foaming character of the surfactant (the cleaning component of the detergent composition), foaming can be quite persistent even during the
10 rinse operation. This results in a number of shortcomings, such as requiring multiple rinses, lengthening the time for the rinse operation, requiring large amounts of water, increasing the amount of waste water, and raising power consumption.

- Various foam control compositions for detergent applications have been disclosed with the goal of excellent cleaning performance while also inhibiting foaming during the post-wash rinsing operation. For
15 example, JP-A 2-230900 discloses a composition having a fatty acid soap as the base component. JP-A 3-269098 describes a composition whose base components are polydimethylsiloxane and hydrophobic silica.

- However those compositions have several deficiencies. For example, large amounts of fatty acid soap must be present to develop the necessary foam-inhibiting performance. This conflicts with the goal of reducing the detergent volume, and also imparts a yellow cast to clothing while the undissolved residues
20 stain the interior of the washing machine. Furthermore, in polydimethylsiloxane-based compositions, the foam-inhibiting activity is lost during the wash stage, which makes it problematic to obtain good performance during rinsing. Although this system can give acceptable performance during rinsing if the polydimethylsiloxane content is raised, this tactic causes excessive foam extinction during the washing stage, to the point that even the foam desirably exhibited by the detergent is almost extinguished.

- 25 The present invention provides a foam control composition comprising 80 to 99 weight% of an organopolysiloxane having amino-functional or carboxyl-functional organic groups and silica having a specific surface area of at least 50 m²/g.

It is an object of the present invention to introduce foam control compositions which permit strong foaming action during the washing stage while inhibiting foaming only during rinsing operations.

- 30 The present invention is a foam control composition comprising (A) 80 to 99 weight% of an organopolysiloxane having the average formula:



- 35 wherein R¹ is selected from hydrogen atom hydroxyl group, and monovalent hydrocarbons having from 1 to 10 carbon atoms, R² denotes a monovalent hydrocarbon having from 1 to 10 carbon atoms, Q denotes a group having the formula -R³Y wherein R³ denotes a divalent hydrocarbon having from 2 to 18 carbon atoms and Y is an amino-functional or carboxyl-functional monovalent organic group, a is zero or greater than zero, b and c are each positive numbers, with the proviso that the sum of a + b + c has a value of
40 1.9 to 2.2, and (B) 1 to 20 weight% of silica having a specific surface area of at least 50 m²/g.

The group R¹ in (A) denotes a hydrogen atom, a hydroxyl group, or a monovalent hydrocarbon group having from 1 to 10 carbon atoms. These monovalent hydrocarbon groups include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, and hexyl; aryl groups such as phenyl, tolyl, and xylyl, aralkyl groups such as benzyl or phenethyl; and haloalkyl groups such as 3-chloropropyl or 3,3,3-trifluoropropyl.

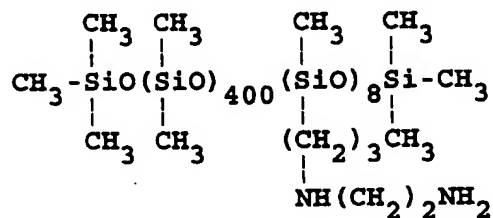
- 45 The group R² denotes a monovalent hydrocarbon group having from 1 to 10 carbon atoms and is exemplified by methyl, ethyl, propyl, butyl, pentyl, hexyl, vinyl, and phenyl.

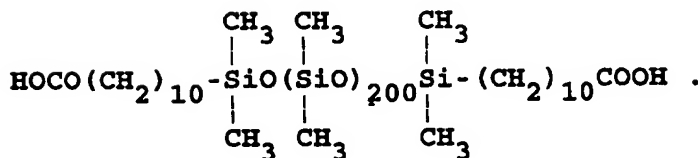
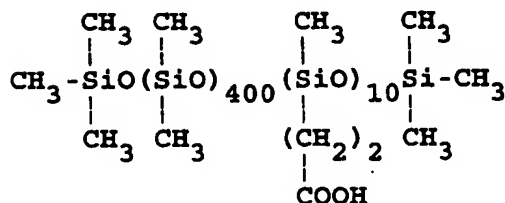
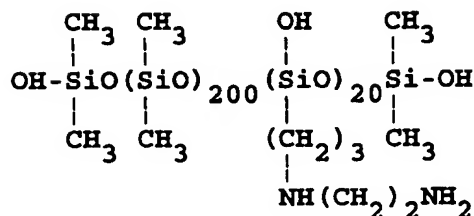
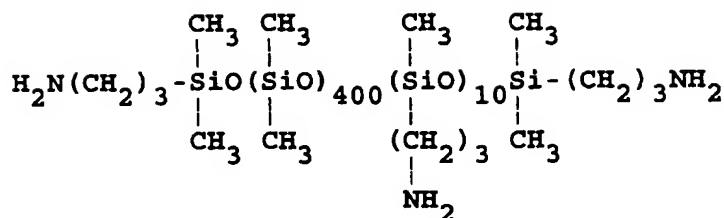
- The group Q is a polar organic group having the formula -R³Y, in which R³ is a divalent hydrocarbon group having from 2 to 18 carbon atoms, for example, ethylene, propylene, butylene, isobutylene, pentamethylene, octamethylene, decamethylene, dodecamethylene, and cyclohexylene. The group Y in
50 -R³Y is an amino-functional or carboxyl-functional monovalent organic group and is exemplified by amino groups including amino, gamma-(2-aminoethyl)amino, methylamino, ethylamino, cyclohexylamino, and phenylamino; a carboxyl group; and alkylthiocarboxyl groups such as methylthiocarboxyl or ethylthiocarboxyl.

- The group Y includes the above amino groups after neutralization with a carboxylic acid, and the
55 carboxyl or thiocarboxyl groups after neutralization with an alkali metal hydroxide or an ammonium compound.

The goal of selectively preventing foaming during the rinsing stage, without adversely affecting the foaming and cleaning performance during the washing action is accomplished when component (A)

preferably has an M/q ratio of 100 to 25,000 and preferably of 200 to 15,000. q is the number of moles of the polar organic group represented by Q in the average component formula $R^1_a R^2_b Q_c SiO_{(4-a-b-c)/2}$, and M is the overall molecular weight of the organopolysiloxane $R^1_a R^2_b Q_c SiO_{(4-a-b-c)/2}$. The polarity is too high when the M/q ratio is less than 100. This causes strong binding to the fabric and interior of the washing machine, which thereby soils the fabric and washing machine, and also prevents the development of an acceptable foam-inhibiting activity. An inadequate polarity is obtained when the M/q ratio exceeds 25,000, which prevents the manifestation of the functional effects of the present invention, i.e., inhibition of foaming only during the rinsing stage without preventing a strong foaming action in the washing stage. Considerations such as processability and dispersibility in the wash bath make viscosities of 50 to 50,000 mm²/s (1 mm²/s = 1 centistoke (cS)) preferred for component (A), while viscosities of 100 to 20,000 mm²/s are more preferred. Component (A) is specifically exemplified by the following compounds:





The foam control compositions of this invention must contain 80 to 99 weight percent of component (A) to exhibit excellent foam-inhibiting performance.

The silica comprising component (B) is added as a foam-inhibiting component, and its specific surface area must be at least 50 m²/g. Silicas having a specific surface area less than 50 m²/g are poorly dispersible in component (A), and also have a poor foam-inhibiting performance. The silica of component (B) is specifically exemplified by fumed silica and calcined silica prepared by dry processes; precipitated silica prepared by wet processes; silica aerogel; quartz; and fused silica. The surface of silica (B) may be treated with silanes or organosiloxane oligomers, either prior to or during its addition to component (A). Silanes used to treat the surface of the silica are exemplified by organoalkoxysilanes such as methyltrimethoxysilane, vinyltrimethoxysilane, and trifluoropropyltrimethoxysilane; organosilazanes such as hexamethyldisilazane; and organohalosilanes such as trimethylchlorosilane and dimethylvinylchlorosilane. The organosiloxane oligomers are exemplified by silanol-endblocked dimethylsiloxane oligomers, silanol-endblocked dimethylsiloxane-methylvinylsiloxane co-oligomers, dimethylhydrogensiloxyl-endblocked dimethylsiloxane oligomers, trimethylsiloxy-endblocked methylhydrogensiloxane oligomers, and trimethylsiloxy-endblocked methylhydrogensiloxane-dimethylsiloxane co-oligomers.

Our foam control composition must contain 1 to 20 weight percent of component (B) to exhibit an excellent foam-inhibiting performance.

These foam control compositions are prepared simply by mixing components (A) and (B) to homogeneity. In addition to components (A) and (B), our foam control compositions may contain optional ingredients such as organopolysiloxanes including trimethylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, trimethylsiloxy-endblocked methylhydrogenpolysiloxanes,

trimethylsiloxy-endblocked methylhydrogensiloxane-dimethylsiloxane copolymers, dimethylhydroxysiloxy-endblocked dimethylpolysiloxanes, dimethylhydrogensiloxy-endblocked dimethylpolysiloxanes, and dimethylsiloxane-methyl(polyoxyalkylene)siloxane copolymers; silicone resins such as triorganosiloxysilicates; and inorganic powders such as aluminum hydroxide, calcium carbonate, and silica other than component (B). The triorganosiloxysilicates may be represented by the formula $[(CH_3)_3SiO_{1/2}]_x[SiO_2]_y$ in which the ratio of x/y ranges from 0.125 to 6. These silicates are prepared by the cohydrolysis of tetraalkoxysilane and trimethylchlorosilane, or by the cohydrolysis of water glass and trimethylchlorosilane in a toluene/water mixture.

The foam control compositions of this invention may be particulate foam control agents in finely divided form for inclusion in a detergent composition in powder form by coating or encapsulation with a carrier substance. The identity of this carrier substance is not critical provided it is soluble or dispersible in water and is solid at room temperature. The carrier substance includes polyethylene glycol, polyethylene glycol-polypropylene glycol copolymers, the alkyl ethers of polyethylene glycol, higher alcohols, higher fatty acid esters, methylcellulose, hydroxymethylcellulose, hydroxycellulose, carboxyvinylcellulose, sucrose fatty acid esters, polyvinyl alcohol, starch, gelatin, and agar. Our foam control compositions may be used after conversion into powder by coating or encapsulation with the carrier substance, wherein said powder may have a flake, spherical, or irregular, morphology.

The devices used to prepare our foam control compositions are not critical, but are preferably capable of simultaneous stirring, heating, and vacuum degassing. Suitable devices are exemplified by homomixers, colloid mills, planetary mixers, kneader mixers, twin-screw extrusion compounders, ball mills, and three-roll mills. An additional increase in the foam-inhibiting performance is obtained by the execution of heat treatment within the range from 30 °C to 200 °C either during or after the mixing of components (A) and (B). To obtain greater effect from this heat treatment, a catalyst, such as sulfuric acid or potassium hydroxide, is preferably added in very small quantities during the heat treatment. Mixing is preferably carried out under an inert gas blanket or reduced pressure as necessary.

In the examples, "parts" indicates "weight parts", the viscosity is the value measured at 25 °C, and viscosity is measured in mm²/s. The foam-inhibiting activity during the wash and rinse stages was tested as follows:

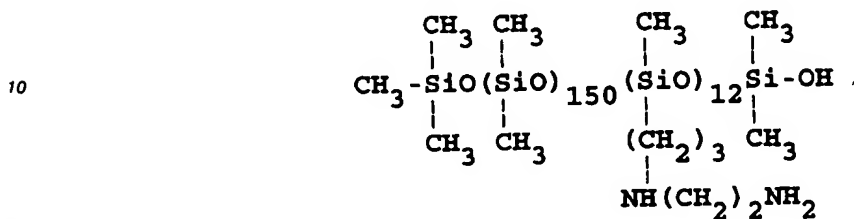
The following were placed in a 50 L 2-tank washing machine (W392 from Matsushita Denki Kabushiki Kaisha): 30 L of water (hardness = 3), 1.2 kg fabric (sports shirts, undershirts, towels), and a commercial granular laundry detergent (Attack from Kao Kabushiki Kaisha) into which the foam control composition had been preliminarily dispersed at the rate of 1.2 weight% based on the quantity of detergent. The foam height was measured after 2 minutes of strong reversing agitation and quiescence for 30 seconds. Agitation was again conducted for 5 minutes, after which the foam height was measured by the same method. This was followed by operation for another 5 minutes and measurement of the foam height. The total of the three foam height values thus obtained was designated as the foam height during the wash stage. The wash water was then discharged over a period of 80 seconds and water (hardness = 3) was introduced up to the level of the overflow discharge on the wash tank. After rinse agitation for 5 minutes and standing for 3 minutes, the foam status on the water surface was evaluated according to the 7-level scale given below, and the resulting value was designated as the foam-inhibiting activity in the first rinse. The rinse water was then discharged over a period of 130 seconds, followed by another rinse using the same procedure. The foam status on the water surface was again evaluated, and the resulting value was designated as the foam-inhibiting activity in the second rinse. The following scale was used to evaluate the foam status on the water surface after each rinse operation.

45	score	foam status on the water surface (area of foam relative to the overall water surface)
	7	foam was not observed on the water surface
	6	a fine foam was observed in the form of several tens of 2 to 3 mm particles (area no larger than about 2%)
	5	a fine foam was observed in the form of islands no larger than 1 cm (area no larger than about 10%)
50	4	a fine foam was observed in the form of islands no larger than several centimeters (area no larger than about 20%)
	3	a layer of fine foam was observed in the form of islands several centimeters in size (area no larger than about 80%)
55	2	a layer of fine foam covered almost the entire surface (area larger than about 80%)
	1	a layer of fine foam covered the entire surface, and foam bubbles were present with diameters greater than or equal to several millimeters

Example 1

A coarse mixture was prepared from the following: 93.5 parts of a dimethylsiloxane-methyl(gamma-(2-aminoethyl)aminopropyl)siloxane copolymer having a viscosity of 1,200 mm²/s and having the average

5 formula:



15

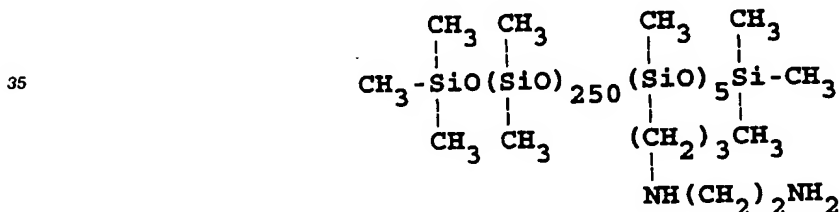
4.5 parts hexamethyldisilazane, 0.4 part ion-exchanged water, and 6.5 parts dry-process silica having a specific surface area of 300 m²/g (Aerosil™ 300 from Nippon Aerosil Kabushiki Kaisha). This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask, where it was reacted at 80°C for 6 hours. The low boilers were subsequently removed by heating to 180°C and stripping for 1 hour at 3.99 kPa(30 mm Hg). Cooling then yielded a silicone foam control composition with a viscosity of 10,000 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

25

Example 2

A coarse mixture was prepared from the following: 93.5 parts of trimethylsiloxy-endblocked dimethylsiloxane-methyl(gamma-(2-aminoethyl)aminopropyl)siloxane copolymer having a viscosity of 1,300 mm²/s

30 having the average formula:



40

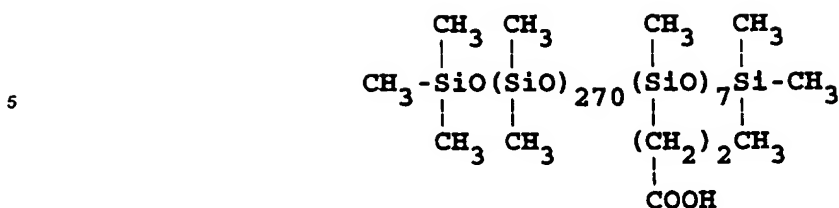
4.5 parts hexamethyldisilazane, 0.4 part ion-exchanged water, and 6.5 parts dry-process silica having a specific surface area of 300 m²/g (Aerosil 300™ from Nippon Aerosil Kabushiki Kaisha). This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask, where it was reacted at 80°C for 6 hours. The low boilers were subsequently removed by heating to 180°C and stripping for 1 hour at 3.99 kPa(30 mm Hg). Cooling then yielded a silicone foam control composition with a viscosity of 6,600 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

50

Example 3

A coarse mixture was prepared from the following: 96 parts of trimethylsiloxy-endblocked dimethylsiloxane-methyl(2-carboxyethyl)siloxane copolymer having a viscosity of 2,300 mm²/s having the average

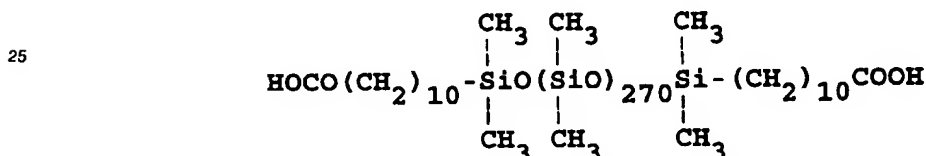
55 formula



10 4 parts dry-process silica having a specific surface area of 300 m²/g (Aerosil 300™ from Nippon Aerosil Kabushiki Kaisha), and 0.03 parts sulfuric acid. This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask, where it was reacted at 150 °C for 2 hours. Cooling then yielded a silicone foam control composition with a viscosity of 25,000 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

Example 4

20 A coarse mixture was prepared from the following: 96 parts of a dimethyl(10-carboxydecyl)endblocked dimethylpolysiloxane having a viscosity of 4,400 mm²/s having the average formula:



30 4 parts dry-process silica having a specific surface area of 300 m²/g (Aerosil 300™ from Nippon Aerosil Kabushiki Kaisha), and 0.03 part sulfuric acid. This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask, where it was reacted at 150 °C for 2 hours. Cooling then yielded a silicone foam control composition having a viscosity of 9,000 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

Comparative Example 1

40 A coarse mixture was prepared from the following: 96 parts trimethylsiloxy-endblocked dimethylpolysiloxane having a viscosity of 5,000 mm²/s, 4 parts dry-process silica having a specific surface area of 300 m²/g (Aerosil 300™ from Nippon Aerosil Kabushiki Kaisha), and 0.03 parts sulfuric acid. This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask, where it was reacted at 150 °C for 2 hours. Cooling then yielded a silicone foam control composition with a viscosity of 9,400 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

Comparative Example 2

50 A coarse mixture was prepared from the following: 88 parts trimethylsiloxy-endblocked dimethylpolysiloxane having a viscosity of 1,000 mm²/s, 10 parts wet-process silica having a specific surface area of 170 m²/g (FK 383 DS™ from the Degussa Corporation), and 2 parts of a solution of trimethylsiloxysilicate having the average formula [(CH₃)₃SiO_{1/2}]_x[SiO₂]_y in which the ratio of x/y was about 0.75. This was followed by processing in a homomixer to obtain a thorough dispersion. This dispersion was transferred into a condenser-equipped four-neck flask. The temperature was raised to 180 °C and a reaction was run for 10 hours at 3.99 kPa (30 mm Hg) with degassing. Cooling and venting to ambient pressure yielded a silicone foam control composition with a viscosity of 3,000 mm²/s. This silicone foam control composition was tested for its foam-inhibiting activity during washing and rinsing, and the results are reported in Table 1.

Table 1
Test Results for Foam Inhibition
During the Wash and Rinse Stages

activity stages	foam height during	foam-inhibiting
	the wash stage	in the rinse
second	(cm)	first
Example 1 6	9	4
Example 2 6	6	4
Example 3 6	2	4
Example 4 5	5	3
Comparative 5 Example 1	1	4
Comparative 6 Example 2	1	4
blank 5	13	1

Claims

1. A silicone foam control composition comprising:

(A) 80 to 99 weight% of an organopolysiloxane having the average formula:



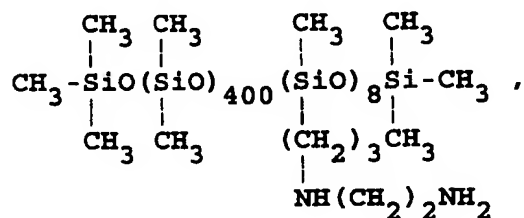
wherein R¹ is selected from hydrogen atom, a hydroxyl group, and a monovalent hydrocarbon group having from 1 to 10 carbon atoms, R² denotes a monovalent hydrocarbon group having from 1 to 10 carbon atoms, Q denotes a group having the formula -R³Y wherein R³ denotes a divalent hydrocarbon group having from 2 to 18 carbon atoms and Y is an amino-functional or carboxyl-functional monovalent organic group, a is zero or greater than zero, b and c are each positive numbers, with the proviso that the sum of a + b + c has a value of 1.9 to 2.2; and (B) 1 to 20 weight% of silica having a specific surface area of at least 50 m²/g.

2. A composition according to Claim 1, wherein R¹ is selected from hydrogen, hydroxyl, methyl, ethyl, propyl, butyl, pentyl, hexyl, phenyl, tolyl, xylyl, benzyl, phenethyl, 3-chloropropyl, or 3,3,3-

trifluoropropyl.

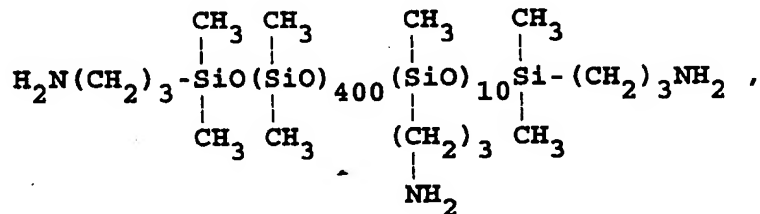
3. A composition according to Claim 1, wherein R² is selected from methyl, ethyl, propyl, butyl, pentyl, hexyl, vinyl, or phenyl.
- 5 4. A composition according to Claim 1, wherein R³ is selected from ethylene, propylene, butylene, isobutylene, pentamethylene, octamethylene, decamethylene, dodecamethylene, or cyclohexylene.
- 10 5. A composition according to Claim 1, wherein Y is selected from amino, gamma-(2-aminoethyl)amino, methylamino, ethylamino, cyclohexylamino, phenylamino, carboxyl, methylthiocarboxyl, or ethylthiocarboxyl.
6. A composition according to Claim 1, wherein (A) is selected from

15



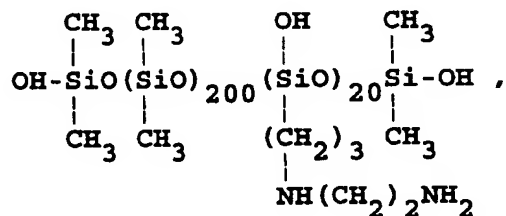
20

25



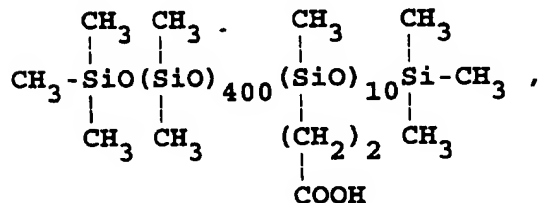
30

35



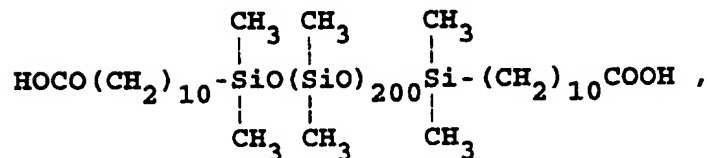
40

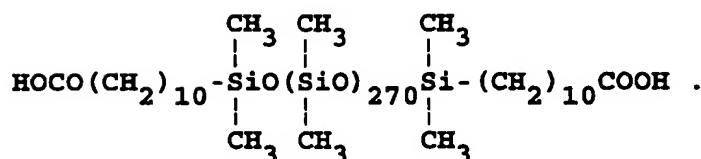
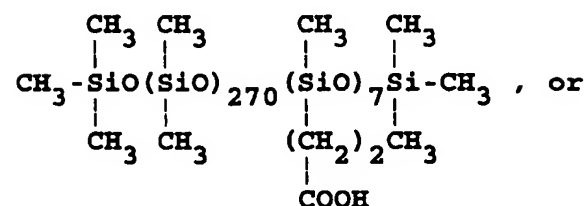
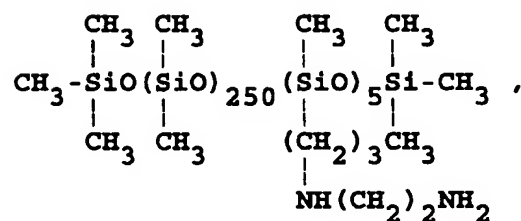
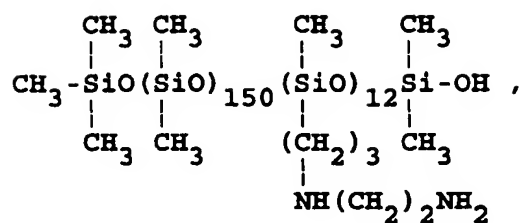
45



50

55





7. A composition according to Claim 1, wherein (B) is selected from fumed silica, calcined silica, precipitated silica, silica aerogel, quartz, and fused silica.
8. A composition according to Claim 1, wherein the composition further comprises a compound selected from organoalkoxysilanes, organosilazanes, organohalosilanes, and organosiloxane oligomers.
9. A composition according to Claim 1, wherein the composition further comprises an organopolysiloxane selected from trimethylsiloxy-endblocked dimethylpolysiloxanes, dimethylvinylsiloxy-endblocked dimethylpolysiloxanes, trimethylsiloxy-endblocked methylhydrogenpolysiloxanes, trimethylsiloxy-endblocked methylhydrogensiloxane-dimethylsiloxane copolymers, dimethylhydroxysiloxy-endblocked dimethylpolysiloxanes, dimethylhydrogensiloxy-endblocked dimethylpolysiloxanes, or dimethylsiloxane-methyl(polyoxyalkylene)siloxane copolymers, silicone resins, or inorganic powders selected from aluminum hydroxide or calcium carbonate.
10. A composition according to Claim 1, wherein the composition further comprises a water soluble or water dispersible carrier.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 10 8233

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 579 999 (GOLDSCHMIDT) * claims 1-7 *	1-10	B01D19/04 C11D3/00 C08L83/08 C08L83/06
X	EP-A-0 427 263 (DOW CORNING) * claims 1-3 *	1-9	
X	EP-A-0 397 297 (UNILEVER) * claim 1 *	1-4, 7, 10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B01D C11D C08L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 August 1995	Examiner Lentz, J
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	